

THE UNIVERSITY OF CHICAGO.

(Founded by John D. Rockefeller.)

ON URETHANES

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE

SCHOOLS OF ARTS, LITERATURE AND SCIENCE

IN CANDIDACY FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

(DEPARTMENT OF CHEMISTRY.)

—BY—

OTTO FOLIN

OCTOBER

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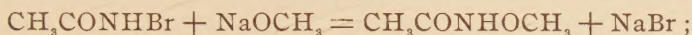
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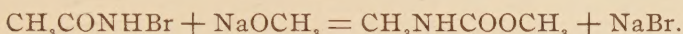
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ON URETHANES.

Sodium methylate and acetbromamide in methyl alcohol solution do not yield a hydroxylamine derivative according to the following equation :

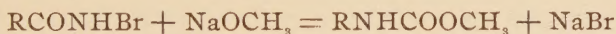


but a molecular rearrangement, analogous to that observed by Hofmann¹ in the action of alkalies on acid bromamides, occurs in the course of the reaction, and a urethane is obtained in place of the isomeric hydroxylamine ether : ²



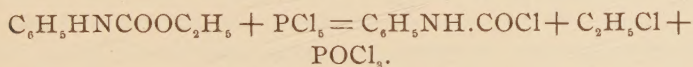
A similar rearrangement occurs in the action of sodium methylate on paranitrobenzbromamide and on succinimide bromide.³

The investigations described in this paper were undertaken at the suggestion of Dr. Stieglitz and Dr. Lengfeld for the purpose of determining whether the reaction



is general, or if it is possible to prevent the rearrangement and effect direct substitution by varying the positive and negative character of the group R.

In the course of their investigations on urethanes, Lengfeld and Stieglitz⁴ obtained chlorformanilide by the action of phosphorus pentachloride on phenylurethane :



The action of phosphorus pentachloride on substituted urethanes, as well as the action of phosphorus pentachloride and

¹ Hofmann : Ber. d. chem. Ges., **14**, 2725 ; **15**, 408, etc.

² Lengfeld and Stieglitz : Am. Chem. J., **16**, 370 ; Stieglitz : *Ibid*, **18**, 752.

³ Am. Chem. J., **15**, 215, 504.

⁴ Am. Chem. J., **16**, 70.

of phosgene on urethane itself was therefore made a part of this investigation in order to test the applicability of the reaction.

I. PREPARATION OF URETHANES FROM ACID BROMAMIDES.

Action of Sodium Methylate on Benzbromamide.

To the cool solution of 1.72 grams sodium in 68 grams pure anhydrous methyl alcohol was added 15 grams benz-bromamide.¹ The bromide dissolved readily, but no reaction occurred in the cold. The solution was boiled on the water-bath for an hour, when a test with potassium iodide and hydrochloric acid showed that no unchanged bromamide remained. After distilling off the greater part of the alcohol, the residue was allowed to evaporate to dryness at ordinary temperatures, and the resulting product extracted with ether.

The ether extract was distilled under reduced pressure and finally recrystallized from hot water. Perfectly white crystals, melting sharply at 47°, were obtained. The compound has the composition and all the properties of methyl phenyl-carbamate, $C_6H_5NHCOOCH_3$, (melting-point 47°). A synthetic preparation of the substance was identical with it in every respect; a mixture of the two melted sharply at 47°.

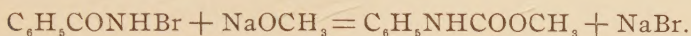
0.1354 gram substance gave 11.65 cc. moist nitrogen at 747 mm. and 24°.

	Calculated for $C_6H_5NO_2$.	Found.
N	9.27	9.53

The main product of the reaction is therefore methyl-phenyl-carbamate. Methyl benzhydroxamate, $C_6H_5CONHOCH_3$, might, however, have been formed by direct substitution to a very slight extent as a by-product. As this substance is somewhat soluble in water, and easily soluble in ether, advantage was taken of these properties to determine whether it is formed at all by the action of sodium methylate on benz-bromamide. 50 grams of the bromamide was treated as described above with the calculated amount of sodium methylate. The hard, dry mass that remained after removing the alcohol

¹ Hoogewerff and Van Dorp: Rec. d. Trav. chim. d. Pays. Bas., 8, 188.

in neutral solution in a vacuum was broken up with the aid of a few drops of ether, and then extracted with water. The extract was repeatedly shaken out with ether; the ethereal solutions dried over potassium carbonate, and the ether distilled off. A small quantity of pure methyl phenylcarbamate remained; hence no methylbenzhydroxamate was formed even as a by-product. No direct replacement of the bromine atom takes place; rearrangement and formation of urethane occur quantitatively according to:



Action of Sodium Methylate on Metanitrobenzbromamide.

Metanitrobenzbromamide was prepared as described by Hoogewerff and Van Dorf.¹ The substance when precipitated by addition of acetic acid to the alkaline solution came down in a very sticky paste. It could be washed only by taking a very small portion at a time, and it was dried on clay plates and in vacuum desiccators over sulphuric acid for seven days before it was perfectly dry.

Methyl m-Nitrophenylcarbamate, $m\text{-NO}_2\text{C}_6\text{H}_4\text{NHCOOCH}_3$.—Two grams sodium (1 atom), dissolved in 80 grams pure methyl alcohol, was heated on the water-bath with 2.15 grams *m*-nitrobenzbromamide (1 molecule) for one hour. A yellow crust formed on the sides of the flask during the heating and, on cooling, a large quantity of a yellow crystalline precipitate was formed. The substance was identified as *m*-nitrophenylmethylurethane. After removing the precipitate by filtration most of the alcohol was distilled off. The mixture changes in color and decomposes on prolonged heating, and the evaporation was, therefore, completed at ordinary temperatures. The residue was extracted with chloroform, and the extract gave by recrystallization from warm chloroform well-formed octahedrons, melting at $147^\circ\text{--}149^\circ$. The compound is *methyl metanitrophenylcarbamate*, $m\text{-NO}_2\text{C}_6\text{H}_4\text{NHCOOCH}_3$, and is obtained in quantities corresponding to 90 per cent. of the theoretical.

¹ Rec. trav. chim., 8, 193.

0.1153 gram substance gave 15.2 cc. moist nitrogen (over 30 per cent. caustic potash) at 743 mm. and at 22°.

N	Calculated for	Found.
	$C_8H_8N_2O_4$	
	14.28	14.66

Methyl metanitrophenylcarbamate, not being known, was prepared synthetically from *m*-nitraniline and methyl chlorformate. It was identical with the body just described.

Action of Sodium Methylate on Orthonitrobenzbromamide.

o-Nitrobenzbromamide has also been prepared by Hoogewerff and Van Dorp.¹ The compound is not so pasty as the meta derivative and can be washed and dried very rapidly.

Methyl-o-Nitrophenylcarbamate, $o\text{-NO}_2C_6H_4NHCOOCH_3$.—10.5 grams *o*-nitrobenzbromamide was added to 1 gram of sodium dissolved in 40 grams methyl alcohol. It dissolved, but no noticeable reaction took place in the cold. The mixture was then heated on the water-bath for twenty minutes. At the end of this time there was no unchanged bromamide left in the solution. The slightly alkaline solution was then acidified with a few drops of dilute acetic acid, and the alcohol allowed to evaporate at ordinary temperatures. The residue, extracted ten times with boiling (40°–50°) ligroïn, gave about 7 grams of a dark yellow oil which, on cooling, solidified. This substance is methyl *o*-nitrophenylcarbamate, mixed with a small quantity of *o*-nitraniline. To remove the latter the mixture was dissolved in pure, cold chloroform and *o*-nitraniline hydrochloride precipitated by means of dry hydrochloric acid gas. The urethane was then precipitated with ligroïn and, after repeated recrystallization from ligroïn, its melting-point was found constant at 53°. *o*-Nitrophenylurethane consists of well-formed greenish-yellow crystals, and is quite soluble in all the ordinary organic solvents except low-boiling ligroïn.

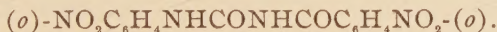
0.2977 gram substance gave 0.5383 gram CO_2 and 0.1192 gram H_2O .

¹ Rec. trav. chim., 8, 191.

	Calculated for $C_8H_8N_2O_4$.	Found.
C	48.98	49.31
H	4.08	4.45

In order to obtain the yield of urethane indicated above (90 per cent.) it is essential that the experiment should be performed as described. As soon as heat is applied to the alcoholic solution of sodium methylate and *o*-nitrobenzbromamide, it turns red and the color deepens as the heating is continued, until at the end of about one hour it is found that the chief product is *o*-nitraniline, most of the urethane evidently being saponified.

As methyl *o*-nitrophenylcarbamate is comparatively unstable at higher temperatures, I attempted to complete the reaction at a temperature below that of boiling methyl alcohol. At 50° I found that the reaction goes about the same as at 66°–70°, and the relative amount of each of the various products obtained varies with the time the heating is continued. At 30°, on the other hand, the result is somewhat different. The reaction proceeded very slowly and was not completed at the end of the fifth hour. The solution remained clear at first, but after a couple of hours, a precipitate, consisting of small white crystals, appeared. This increased constantly in amount until it was removed by filtration at the end of five hours, after which the reaction was completed by boiling on the water-bath for fifteen minutes. The precipitate melted at 220°. It is insoluble in all the ordinary organic solvents except acetone. The same compound was obtained in larger quantities by Swartz,¹ who also made a closer investigation of it, and by analysis and synthesis showed it to be *o*-nitrophenyl-*o*-nitrobenzoylurea,



The substance obtained in this reaction is in every respect identical with the synthetic product prepared by Swartz. Its formation here is due to the reducing action of methyl alcohol on a part of the *o*-nitrobenzbromamide, giving formaldehyde and

¹ Am. Chem. J., 19, 295.

o-nitrobenzamide, the latter of which is then acted upon by a molecule of *o*-nitrophenyl isocyanate, formed by the rearrangement of a second molecule of *o*-nitrobenzobromamide.¹ The odor of the aldehyde was quite distinct.

1. $\text{NO}_2\text{C}_6\text{H}_4\text{CONHBr} + \text{NaOCH}_3 = \text{NO}_2\text{C}_6\text{H}_4\text{CONH}_2 + \text{CH}_2\text{O} + \text{NaBr}.$
2. $\text{NO}_2\text{C}_6\text{H}_4\text{CONHBr} + \text{NaOCH}_3 = \text{NO}_2\text{C}_6\text{H}_4\text{N}=\text{CO} + \text{NaBr} + \text{HOCH}_3.$
3. $\text{NO}_2\text{C}_6\text{H}_4\text{N} = \text{CO} + \text{NH}_2\text{COC}_6\text{H}_4\text{NO}_2 = \text{NO}_2\text{C}_6\text{H}_4\text{NHCONHCOC}_6\text{H}_4\text{NO}_2.$

Action of Sodium Methylate on Metabrombenzobromamide.

Pure *m*-brombenzoic acid was converted successively with phosphorus pentachloride and ammonia into the acid chloride and *m*-brombenzamide. The latter crude product was not perfectly white, but it was quite pure and had a melting-point somewhat higher than that found by Engler,² 150°. Recrystallized from chloroform, it was obtained in perfectly white crystals, melting at 153°-4°. Analysis showed its purity :

0.2014 gram substance gave 12.6 cc. moist nitrogen at 740.3 mm. and 21°.

	Calculated for $\text{C}_7\text{H}_5\text{NOBr}.$	Found.
N	7.00	6.97

Metabrombenzobromamide, *m*- $\text{BrC}_6\text{H}_4\text{CONHBr}$.—This bromide was not known ; but it was prepared from the amide by exactly the same method as that used by Hoogewerff and Van Dorp in the preparation of the nitrobenzobromamides. The yield was good. The compound was slightly colored and consisted of prismatic, microscopic needles, melting at 105°. The bromine attached to the nitrogen was determined in the crude product, and no attempt was made to obtain it in perfectly pure condition :

	Calculated for $(\text{C}_7\text{H}_5\text{BrON})\text{Br}.$	Found.
Active bromine	28.7	27.9

¹ Hofmann : Ber. d. chem. Ges., 14, 2725 ; Lengfeld and Stieglitz : Am. Chem. J., 15, 506 ; Stieglitz : *Ibid.*, 18, 752.

² Ber. d. chem. Ges., 4, 708.

Methyl Metabromphenylcarbamate, $m\text{-BrC}_6\text{H}_4\text{NHCOOCH}_3$.

—Five grams *m*-brombenzobromamide was added to 0.4 gram sodium dissolved in 20 grams absolute methyl alcohol, and the mixture heated for one hour. The solution was neutralized and the greater part of the alcohol distilled off. On adding water to the remainder, a white precipitate came down. This was recrystallized from chloroform by the addition of ligroin and analyzed.

0.2678 gram substance gave 15.25 cc. moist nitrogen at 749.3 mm. and 25°.

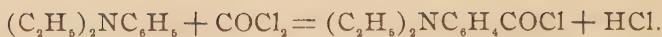
	Calculated for $\text{C}_8\text{H}_8\text{NO}_2\text{Br}$.	Found.
N	6.09	6.29

Methyl *m*-bromphenylcarbamate is a white crystalline compound melting at 84.5°–85.5°; insoluble in water and soluble in all the ordinary organic solvents except ligroin. The yield of urethane in the above reaction is from 80 to 90 per cent. of the theoretical, and the remainder of the bromamide is reduced to the amide and is recovered.

As the work just described shows that the rearrangement of the acid bromamides, RCONHBr , occurs almost quantitatively, even when R is strongly negative ($\text{R} = \text{C}_6\text{H}_5$; $o\text{-NO}_2\text{C}_6\text{H}_4$; $m\text{-NO}_2\text{C}_6\text{H}_4$; $m\text{-BrC}_6\text{H}_4$), the effect of positive radicals was studied. A dialkylamidobenzamide, $\text{R}_2\text{NC}_6\text{H}_4\text{CONH}_2$, was first chosen rather than an amidobenzamide in order to remove the possibility of the hypobromite acting on the amide group attached to the benzene ring, in preparing the bromamide. As no such amides had been prepared and described, a few experiments were first made to determine the best method for obtaining them.

p-Diethylamidobenzamide, $p\text{-(C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{CONH}_2$.—Michler obtained dimethylamidobenzoic acid by heating dimethylaniline and phosgene in sealed tubes to 50° and pouring the resulting mixture into water.¹ To prepare the amide 62 grams phosgene was passed into 95 grams diethylaniline in a flask attached to an inverted condenser cooled with a freezing-mixture. The two reacted slowly, the mixture gradually solidifying to a white mass, which was colored first red and later a deep blue :

¹ Ber. d. chem. Ges., 9, 400, etc.

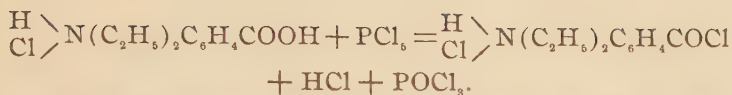


The crude chloride thus formed was slowly added to an excess of strong, cold ammonia. The reaction was quite violent; but only 12 grams of the expected acid amide was obtained, the greater portion of the acid chloride being converted into diethylamidobenzoic acid instead. The amide obtained in this reaction is not pure. It is mixed with benzophenone derivatives, and a blue coloring matter, which can be removed only very slowly and with great loss by fractional precipitation from hot alcohol.

Since diethylamidobenzoic acid is easily purified, it was thought best first to prepare this pure, and then convert it by means of phosphorus pentachloride and ammonia into the amide. The acid was prepared by Michler's method and purified by dissolving in alkalies and reprecipitating the acid with acetic acid (melting-point 188°).

Action of Phosphorus Pentachloride on p-Diethylamidobenzoic Acid.—Phosphorus pentachloride and diethylamidobenzoic acid were mixed in molecular quantities. Action set in only with great difficulty at 60° – 70° , and the mass became very brown as the reaction proceeded. The amide obtained by the action of ammonia on this product was quite impure. A very smooth reaction can be brought about by first passing dry hydrochloric acid into a chloroform solution of diethylamidobenzoic acid, thus converting it into the hydrochloride, $\text{HCl}(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{COOH}$, before adding phosphorus pentachloride. Reaction with the latter now sets in at once at 40° – 50° , a clear, colorless mixture of phosphorus oxychloride and the hydrochloride of diethylamidobenzoic acid chloride being obtained. This behavior of diethylamidobenzoic acid toward phosphorus pentachloride is further evidence that it is really a salt, perhaps $\text{HN}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_4\text{COO}$, which like other salts,

would not react so readily with phosphorus pentachloride. The hydrochloride, $\text{ClHN}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_4\text{COOH}$, is a true acid and reacts as smoothly with phosphorus pentachloride as any other acid:



The acid chloride thus obtained gives, with ammonia, diethylamidobenzamide in very pure condition, with a yield of 50 per cent. Considerable quantities of regenerated acid were always recovered from the ammoniacal filtrate, with only slight loss of material.

p-Diethylamidobenzamide is a white crystalline solid melting at 136°–137°. It is readily soluble in hot water and in hot alcohol, but is very little soluble in any of the other organic solvents.

0.1878 gram substance gave 24.2 cc. moist nitrogen at 740 mm. and 17°.

	Calculated for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}$.	Found.
N	14.58	14.61

Ethyl Diethylamidobenzoate, $(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{COOC}_2\text{H}_5$. — In place of converting diethylamidobenzoic acid into the amide by means of its chloride, an attempt was made to prepare it from its ester. The best yield of ethyl diethylamidobenzoate (75 per cent.) was obtained by dissolving the acid in alcohol and heating it with from 4 to 5 equivalents of sulphuric acid on the water-bath for ten hours. Ethyl diethylamidobenzoate is described by Michael and Wing as an oil which solidifies in a freezing-mixture, but melts again at ordinary temperatures.¹ I found it to be a white solid consisting of irregular rhombohedral plates, insoluble in water and very soluble in ether and chloroform. It was repeatedly recrystallized from hot alcohol until it melted sharply at 43°.

0.2942 gram substance gave 0.7616 gram CO_2 and 0.2464 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{19}\text{NO}_2$.	Found.
C	70.60	70.59
H	8.6	9.31

Ethyl Diethylamidobenzoate and Ammonia. — From the ester thus prepared I was unable to get the corresponding amide by treatment with ammonia. The ethyl diethylamidobenzo-

¹ Am. Chem. J., 7, 197.

ate was heated with a large excess of aqueous ammonia and with alcoholic ammonia on the water-bath; it was left in glass-stoppered bottles with concentrated aqueous ammonia and with saturated alcoholic ammonia for several weeks, but not a trace of the acid amide was obtained. The ester remained unchanged.

The yield of diethylamidobenzamide obtained from diethylaniline by way of diethylamidobenzoic acid being rather unsatisfactory, a better yield of such an amide was sought by converting dimethylaniline into an amide by means of the nitrile, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CN}$.

Action of Cyanogen Bromide on Dimethylaniline.—As the hydrogen atom in the para position to the amide group in dimethylaniline is very easily replaced, the latter might, it seemed, be converted by the action of cyanogen bromide into dimethylamidobenzonitrile. Dimethylaniline in dry chloroform solution was first converted into its hydrochloride and mixed with one molecule of cyanogen bromide. Aluminium chloride was then added, a small portion at a time; it produced a lively reaction in the mixture. All but the aluminium chloride went into solution. The latter was removed by filtration; the filtrate distilled, and the solid residue distilled with steam. A crystalline solid came over, which was soluble in all the organic solvents and melted at 55° – 56° . The melting-point and all the properties of the compound correspond to those of parabromdimethylaniline. It was prepared synthetically and the two were identical.

The reaction, therefore, did not take place as was expected and the bromine, instead of the cyanogen radical, was found to have replaced the para hydrogen atom in dimethylaniline.



Action of Cyanogen Bromide on Parabromdimethylaniline.—Cyanogen bromide failing to give the nitrile by acting on dimethylaniline, its action on *p*-bromdimethylaniline in the presence of sodium was tried, in the attempt to fulfil the equation:¹



¹ Claus: Ber. d. chem. Ges., 16, 915.

2.75 grams sodium wire in 100 grams absolute ether was cooled in a freezing-mixture. 12 grams *p*-bromdimethylaniline¹ and 6.26 grams cyanogen bromide were mixed and added to the sodium in the ether.

Both bodies dissolved in the ether, but no reaction took place until the flask was taken out of the freezing-mixture. The reaction was very rapid, as the contents of the flask began to get a little warmer, but was easily regulated by cooling. After the reaction was completed, a solid containing only sodium bromide and sodium cyanide was removed by filtration and the ether distilled off. The remaining residue was found to be only unchanged *p*-bromdimethylaniline. The cyanogen bromide, therefore, is decomposed by the sodium and no nitrile is obtained.

p-Dimethylamidobenzonitril, $p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CN}$.—By treating the diazochloride of *p*-amidodimethylaniline with Sandmeyer's potassium cyanide-copper sulphate solution, Ahrens² obtained an oil from which he was unable to isolate the nitrile, but which gave dimethylamidobenzoic acid with alcoholic potash, proving the presence of the nitrile. No statement of the yield being made, Ahrens' work was repeated by me.

The oil described by him was obtained, and was distilled with steam. At first a colorless oil came over which was found to be dimethylaniline. Afterwards a light-colored substance was carried over, which solidified in the condenser. It was purified by precipitating it from ether solution with ligroïn, and thus obtained in slightly yellowish needles, which melted at 74°–76°. It is very soluble in chloroform and ether, and very little soluble in low-boiling ligroïn. By prolonged boiling with strong alcoholic potash it is converted into *p*-dimethylamidobenzoic acid (melting-point 235°). Its properties show it to be *p*-dimethylamidobenzonitrile, but the yield was too small to make its preparation an advantageous one for the purpose of obtaining a dialkylamidobenzamide. These are therefore best prepared from the dialkylamidobenzoic acids by the successive action of hydrochloric acid, phosphorus pentachloride, and ammonia, as described above.

¹ Weber: Ber. d. chem. Ges., 8, 715; 10, 763. ² Ber. d. chem. Ges., 20, 2958.

Action of Potassium Hypobromite on p-Diethylamidobenzamide.—One gram diethylamidobenzamide was added to a cold solution containing the calculated quantity of potassium hypobromite. A part of the amide dissolved, and a precipitate was formed which quickly changed to a dark-brown color. The solution was filtered and cold boric acid added to the filtrate. A brown sticky precipitate resembling the first one was thrown down. It dissolved in hydrochloric acid and was again precipitated with ammonia; but it did not give off bromine with the acid or nitrogen with ammonia. The dry substance gave a very distinct dark green flame when ignited with copper oxide, and was probably some compound containing one or more bromine atoms in the benzene ring. It certainly was not diethylamidobenzbromamide, $(C_2H_5)_2NC_6H_4CONHBr$. As acid chloramides are rather more stable than the corresponding bromamides, diethylamidobenzamide was allowed to react with molecular quantities and with excess of hypochlorous acid. A yellow, sticky precipitate was extracted with ether, and a substance obtained which gave the test for halogen amide with potassium iodide and hydrochloric acid when freshly prepared; but it rapidly decomposed, and when left over night it no longer gave the test for halogen amide. On account of this instability of the halogen amides, $R_2NC_6H_4CONHX$, the action of sodium methylate on them could not be investigated.

Action of Hypobromite on Metamidobenzamide.—Another attempt was made with metamidobenzamide. This amide was treated with cold potassium hypobromite solution in the usual manner. A reddish precipitate was obtained which, when placed on clay plates, soon turned to a black amorphous mass, containing bromine and not melting below 280° . The experiment was repeated in various ways, but with no better results. The black amorphous mass was extracted with ether, alcohol and chlorform in a Soxhlet apparatus; but each extract was amorphous, and no definite product was isolated. Several of these extracts, as well as the residue, were heated in sealed tubes with hydrochloric acid and the products examined for metaphenylenediamine, but none was found.

Having thus failed to obtain an acid bromamide containing the amido or dialkylamido groups in the benzene ring, probably on account of the remarkable reactivity which such positive groups give to the benzene ring, I succeeded in preparing an analogous acid bromamide in the aliphatic series, on which the action of sodium methylate was tried. Carbomethoxy- β -amidopropionamide, $\text{CH}_3\text{O}_2\text{CNHCH}_2\text{CH}_2\text{CONH}_2$, was selected because it can be prepared without much difficulty.¹

Carbomethoxy- β -amidopropionbromamide, $\text{CH}_3\text{O}_2\text{CNHCH}_2\text{CH}_2\text{CONHBr}$.—Two grams caustic potash was dissolved in a very small quantity of water, and 2.1 grams bromide added at -5° , and to this cold solution was added 2 grams carbomethoxy- β -amidopropionamide. The latter dissolved in a few minutes. Cold acetic acid was next added in slight excess without letting the temperature of the mixture rise above -5° . The acetic acid does not precipitate the bromamide at once, as it does in the precipitation of the aromatic ones; but in a few minutes the precipitate begins to form and then comes down very rapidly. The yellow crystalline bromamide was rapidly filtered and washed with a small quantity of cold water. It is easily soluble in water and no attempt was made to obtain it in perfectly pure condition. By using very small quantities of cold water a good yield of bromamide (80 per cent. pure) was obtained. Crude carbomethoxy- β -amidopropionbromamide is a white crystalline compound and melts with decomposition at 117° – 118° .

Action of Sodium Methylate on Carbomethoxy- β -amidopropionbromamide.

0.4 gram sodium was dissolved in 20 grams absolute methyl alcohol and 4.5 grams carbomethoxy- β -amidopropionbromamide added. The latter dissolved and the mixture was boiled half an hour, when no bromamide was left unchanged. The solution was carefully neutralized with acetic acid and the mixture allowed to evaporate to dryness in a vacuum-desiccator. The white solid mass that remained was extracted with chloroform, and the chloroform solution washed

¹ Lengfeld and Stieglitz : Am. Chem. J., 15, 512.

with small quantities of dilute hydrochloric acid, caustic soda solution and water. The solution was then dried over calcium chloride, and the chloroform distilled. An oil remained which solidified as soon as it began to cool. The weight of this solid was only 0.3 gram. Some was undoubtedly removed by the repeated washings of the chloroform solution; but the main object sought was purity of substance rather than a larger yield. It was recrystallized from dilute alcohol and from water, giving 0.2 gram of a compound melting at 132° – 3° . The melting-point, crystalline form and solubilities of this compound are the same as those ascribed by Franchimont and Klobbie¹ to the dimethyl ester of ethylenedicarbamic acid, $\text{CH}_3\text{O}_2\text{CNHCH}_2\text{CH}_2\text{NHCO}_2\text{CH}_3$.

0.1484 gram substance gave 22 cc. moist nitrogen at 744 mm. at 24° .

	Calculated for $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$.	Found.
N	15.91	16.35

The usual rearrangement,



occurs, therefore, in this case; but exactly what yield of urethane can be obtained, or what other products are formed, was not investigated on account of the small amount of material on hand.

The above experiments show that the reaction,



is quite general, as it succeeded with all acid bromamides that could be isolated and investigated.

II. ACTION OF PHOSPHORUS PENTACHLORIDE ON URETHANES.

Action of Phosphorus Pentachloride on Phenylurethane.

Lengfeld and Stieglitz² obtained, by the action of phosphorus pentachloride on 10 grams phenylurethane, about 3 grams chlorformanilide,



The chief reason why a larger yield was not obtained

¹ Rec. d. trav. chim. Phys. Bas., 7, 258. ² Am. Chem. J., 15, 71.

seems to be that a part of the chlorformanilide at the temperature of the reaction (50° – 60°) lost hydrochloric acid giving phenyl isocyanate, which is quite soluble in ligroin.¹ The reaction of phosphorus pentachloride and phenylurethane was repeated under somewhat different conditions to improve the yield.

6.25 grams phosphorus pentachloride and 5 grams urethane gave 1.5 grams chlorformanilide after removing the phosphorus oxychloride with ligroin (boiling-point 40° – 60°). The mixed liquids were transferred from the solid precipitate into another flask and dry hydrochloric acid was then passed through the mixture. In a few minutes crystals began to appear. The current of hydrochloric acid was continued for about half an hour, the ligroin being renewed from time to time. 0.8 gram chlorformanilide was thus obtained, increasing the yield, therefore, over fifty per cent. The best conditions for preparing chlorformanilide were found to be as follows:

10 grams urethane was acted upon by 12.5 grams phosphorus pentachloride. Pure, dry chloroform was then added in small quantity, and hydrochloric acid gas passed through the solution at ordinary temperatures until nearly all the phosphorus oxychloride had been driven off, the chloroform being renewed as fast as it was removed. The dissociation into the volatile isocyanate and hydrochloric acid is diminished by the stream of hydrochloric acid gas, and chlorformanilide, not being volatile at ordinary temperatures, remains. The latter was then precipitated as before by the addition of low-boiling ligroin and nearly 6 grams, or about 60 per cent. of the theoretical yield, was obtained, which is almost twice as much as was obtained without the addition of dry hydrochloric acid.

Action of Phosphorus Pentachloride on Metanitrophenylurethane.

8.5 grams *m*-nitrophenylurethane and 8.5 grams phosphorus pentachloride were heated together in a dry flask to 55° – 65° . No reaction took place until some of the urethane was brought into solution by the addition of a little dry chloroform. The

¹ Werner: Ber. d. chem. Ges., **26**, 1565; Hentchel: *Ibid*, **18**, 1178.

reaction-product was cooled in a freezing-mixture and dry hydrochloric acid passed through. In a few minutes a white crystalline solid appeared, and increased rapidly until the whole of the contents in the flask solidified. More chloroform was added, and was driven off by a continuous, strong stream of hydrochloric acid, in order to carry off most of the phosphorus oxychloride. Cold ligroïn was added and the precipitate rapidly filtered and washed. 6.6 grams *m*-nitrophenylurea chloride or 81 per cent. of the theoretical yield was obtained. Chlorformmetanitrilide is a nearly colorless crystalline solid, which melts at 102° with decomposition.

I. 0.2956 gram substance gave 0.04895 gram chlorine.

II. 0.2877 gram substance gave 0.04772 gram chlorine (Volhard).

	Calculated for $C_7H_5N_2O_3Cl$.	I.	Found.	II.
Cl	17.72	16.56		16.59

Urea chlorides decompose readily, losing hydrochloric acid, and hence the figures are low.

Metanitrophenylurea, $m\text{-NO}_2C_6H_4NHCONH_2$.—In order more fully to identify the urea chloride obtained in the last experiment, a small amount of it was added to ammonia. It reacted violently, and a yellow crystalline solid was formed, which after recrystallization from hot water, melted at 195° , with slight decomposition. Hofmann¹ describes *m*-nitrophenylurea as consisting of long yellow needles. If the hot water solution is allowed to cool very slowly the substance does come down as described by Hofmann; but if rapidly cooled, it comes down in plates.

0.1788 gram substance gave 36 cc. moist nitrogen at 746 mm. and 19° .

	Calculated for $C_7H_7N_3O_3$.	Found.
N	23.20	23.06

Metanitrophenyl Isocyanate, $m\text{-NO}_2C_6H_4NCO$.—Metanitrophenylurea chloride was heated in a current of dry air to 110° – 140° until no trace of hydrochloric acid could be detected in the air that had passed through the apparatus. The residue

¹ Ann. Chem. (Liebig), **67**, 156; **70**, 137.

was then extracted with sodium-dried ligroin. The isocyanate is quite soluble in boiling ligroin, and on cooling it comes down as a microcrystalline, inodorous, white solid, melting at 49°–50°.

0.1957 gram substance gave 30.9 cc. moist nitrogen at 741 mm. and 23°.

	Calculated for $C_7H_4N_2O_3$.	Found.
N	17.08	17.33

Metanitrophenyl isocyanate has all the characteristics of phenyl isocyanate, except the odor, and readily gives the usual isocyanate addition-products. Methylnitrophenylurethane, $m\text{-NO}_2C_6H_4NHCOOCH_3$, (melting-point 148°) was obtained by the action of isocyanate on absolute methyl alcohol. The corresponding ethylurethane¹ (melting-point 63°) was similarly obtained from ethyl alcohol. With ammonia the reaction is very violent, giving the *m*-nitromonophenylurea just described above.

Metanitrophenyl-m-nitrobenzoylurea, $m\text{-NO}_2C_6H_4NHCONHCOC_6H_4NO_2\text{-}m$.—Molecular quantities of metanitrophenyl isocyanate and *m*-nitrobenzamide were heated to 150°. The melted mixture soon solidified and the product was found to be *m*-nitrophenyl-*m*-nitrobenzoylurea, melting at 230°.



This urea is isomeric with the corresponding ortho derivative obtained by me as a by-product in the action of sodium methylate on orthonitrobenzobromamide.

0.1577 gram substance gave 24.9 cc. moist nitrogen at 740 mm. and 24°.

	Calculated for $C_{14}H_{10}N_4O_6$.	Found.
N	16.97	17.32

Action of Phosphorus Pentachloride on Metabromphenylurethane.

Metabromphenylurethane reacted with phosphorus pentachloride quite as readily as did the *m*-nitrophenylurethane and a good yield of white, crystalline *m*-bromphenylurea chloride, $m\text{-BrC}_6H_4NHCOCl$, was obtained.

¹ Struve und Radenhausen: J. prakt. Chem., **52**, 230. They give the melting-point 56°. Swartz: Am. Chem. J., **19**, 295, found the melting-point 65°.

The compound was identified by treating it with strong ammonia thus producing

Metabromphenylurea, *m*-BrC₆H₄NHCONH₂. — *m*-Brom-phenylurea is very little soluble in all the ordinary organic solvents except alcohol. It was purified by dissolving an absolute alcohol and precipitating with ether and ligroin. White needles, softening at 162°, melting at 164°–5°.

0.1514 gram substance gave 18.15 cc. moist nitrogen at 742 mm. and 25.3°.

	Calculated for C ₇ H ₇ N ₂ OBr.	Found.
N	13.02	13.12

These experiments show that with urethanes of the aromatic amines the reaction,

$\text{RNHCOOCH}_3 + \text{PCl}_5 = \text{RNHCOCI} + \text{CH}_3\text{Cl} + \text{POCl}_3$,
is general. Methyl chloride is first split off, giving chlorformanilides which are easily isolated, and from which the isocyanates can readily be obtained by the further loss of hydrochloric acid.

Phenyl isocyanate and chlorformanilide, hitherto prepared from aniline and phosgene, can be more conveniently prepared, especially in moderate quantities, by the method just described.¹ And since metanitrobenzoic acid is easily available, and can be readily converted into methyl *m*-nitrophenyl-carbamate and its chloride, the latter may often be conveniently used in place of phenyl isocyanate, the melting-points of its derivatives being 15° to 100° higher.

Whether the above reaction is also applicable to the urethanes of the aliphatic amines and to urethane itself remained to be ascertained. I have studied the action of phosphorus pentachloride on urethane.

Preparation of Urethane.

Liebig and Wöhler² passed isocyanic vapors into a mixture

¹ In making the urethanes it is not necessary to isolate the bromamides. As has been found by Miss Jeffreys, working under the direction of Dr. Stieglitz, a mixture of the acid amide and bromine dissolved in methyl alcohol may be treated with the solution of sodium methylate, or bromine may be added to such a solution of the amide and the methylate. In this way the urethanes can be prepared from many acid amides in good yield in one to two hours. Miss Jeffreys will report later on this reaction in the *American Chemical Journal*. ² *Ann. Chem. (Liebig)*, **54**, 370; **58**, 260.

of alcohol and ether and obtained in addition to allophanic ethylester small quantities of urethane. The use of potassium isocyanate and hydrochloric acid in place of the isocyanic acid vapors for the preparation of urethane seems never to have been tried. Amato¹ obtained allophanic ether from such a mixture of potassium isocyanate, alcohol, and dilute hydrochloric acid by boiling two days.

A good yield of urethane can nevertheless be obtained from just such a mixture by proceeding as follows: 5 grams potassium isocyanate was dissolved in just enough dilute (50 per cent.) warm alcohol to make a clear solution. This was then slowly added to a strong alcoholic solution of hydrochloric acid containing an excess of acid. The reaction is completed only very slowly on account of the insolubility of potassium isocyanate in alcohol, and the mixture was left standing at ordinary temperatures till the following day. A white precipitate was formed when the two solutions were mixed, and after twenty-four hours it gave off no gas when treated with aqueous hydrochloric acid. The excess of hydrochloric acid was neutralized with barium carbonate, the mixture filtered, and most of the alcohol removed by distillation. The remainder was allowed to evaporate to dryness in a vacuum-desiccator. The residue, extracted with ether, gave, after drying and distilling off the ether, 3.3 grams urethane, corresponding to a yield of 60 per cent. Urethane is quite volatile, and it was found by experiment that a considerable quantity is carried over by the alcohol when the latter is removed by distillation. Such losses could undoubtedly be avoided, and the above yield largely increased by using a Hempel tube in distilling off the alcohol.

Action of Phosphorus Pentachloride on Urethane.

10 grams (1 molecule) urethane and 23.3 grams phosphorus pentachloride (1 molecule) were mixed and at once began to react with evolution of a considerable amount of gas and with the absorption of so much heat that the flask containing the mixture became quite cold. In twenty minutes the reaction seemed to be complete, leaving a clear, colorless liquid in the

¹ Jsb. d. Chem., 1873, 749.

flask. Gattermann,¹ who prepared carbamic acid chloride, NH_2COCl , by the action of phosgene on ammonium chloride describes it as a white, crystalline body, insoluble in ligroïn, melting at 50° and boiling at 61° – 62° . Dry ligroïn produced, however, no precipitate in the above liquid, even when cooled in a freezing-mixture. The ligroïn solution was slowly added to cold aniline, and the resulting white, solid mixture carefully examined for monophenylurea, but none was found.

The gas given off in the cold consists chiefly of hydrogen chloride but, on heating, much ethyl chloride escapes. The reaction was repeated in a current of dry hydrogen chloride, and the mixture distilled at 40 mm. in a current of hydrogen chloride, which was intended to decrease possible loss of chlorformamide by dissociation.² The distillate was collected in several different fractions, each of which reacted violently with water, giving carbon dioxide in quantities of only 44 to 66 per cent. of the theoretical for chlorformamide. With aniline no phenylurea could be obtained, with methyl alcohol no methylurethane, all of which experiments show that by the action of phosphorus pentachloride on urethane, unlike that on phenylurethane, no chlorformamide is formed. A final effort to show its presence was based on the fact that chlorformamide very readily gives with urethane ethyl allophanate,³ which is easily isolated and recognized. A portion of the distillate mentioned was added to an ethereal solution of urethane. No reaction took place until after the ether had been distilled off and the heating on the water-bath continued for ten minutes. After the evolution of hydrochloric acid, which further heating produced, had ceased, the mixture solidified on cooling. This solid, washed and dried, melted at 190° . After recrystallization it was analyzed and found to be ethyl allophanate.

0.2420 gram substance gave 47 cc. moist nitrogen at 742 mm. and 24.5°

	Calculated for $\text{C}_4\text{H}_8\text{N}_2\text{O}_3$.	Found.
N	21.21	21.30

¹ Ann. Chem. (Liebig), **244**, 29.

² Gattermann : *Ibid.*

³ Gattermann : *Ibid.*

As Schroeter and Livinsk¹ had attempted to prepare allophanic ether by the action of phosphorus oxychloride on urethane, and had found that none was formed, it seemed here that the formation of allophanic ether must have been due to the presence of chlorformamide in the above distillate. It was thought best, however, to repeat the work of Schroeter and Livinsk and, on heating molecular quantities of urethane and phosphorus oxychloride on the water-bath, I obtained quite different results from those published by these chemists. Hydrochloric acid soon began to come off, and, on removing the unchanged urethane and phosphorus oxychloride with water, a residue remained from which allophanic ether was obtained and identified as usual.

The formation of allophanic ether in the action of urethane on the unknown chloride obtained by distilling a mixture of urethane and phosphorus pentachloride does, therefore, not prove the presence of chlorformamide in the distillate, while the other experiments described leave little doubt that no chlorformamide is formed in the reaction. From the results of a study of the action of phosgene on urethane, which will presently be described, and which showed the amide group in urethane to be most sensitive to reaction, it seems probable that when phosphorus pentachloride acts on urethane, besides forming as with other urethanes the chlorformamide complex, it introduces at the same time a phosphoric acid radical into the amide group, giving derivatives of the nature of, *e. g.*, $\text{Cl}_2\text{P}(\text{NHCOC}\text{Cl})_2$ or $\text{Cl}_2\text{PO}(\text{NHCOC}\text{Cl})$, etc. Such substances would give carbon dioxide with water, (40–70 per cent. as much as an equal weight of chlorformamide) and would give no phenylurea with aniline, nor urethane with alcohol.

III. ACTION OF PHOSGENE ON URETHANE.

One of the chief difficulties encountered in the study of the action of phosphorus pentachloride on urethane being the removal of phosphorus oxychloride from the reaction-product, phosgene, which has been used in similar cases² in place of phosphorus pentachloride because it gives only gaseous by-products, was brought into action with urethane. Its action

¹ Ber. d. chem. Ges., 26, 2171.

² Kempf: J. prakt. Chem. [2], 1, 402.

on urethane might be analogous to the action of phosphorus pentachloride on phenylurethane, and thus give chlorformamide :



The only previous work¹ done on the action of phosgene on urethane rather indicated that such is the primary reaction. Loeb obtained from phosgene in benzene solution and a large excess of urethane, allophanic ether, as sole product, the very substance which chlorformamide forms in presence of an excess of urethane.²

Loeb, in the brief notice he published on the reaction, suggested that the allophanic ether could be formed by abstracting one molecule of alcohol from two molecules of urethane without indicating in what way such a reaction might take place. He also suggested another explanation for the formation of allophanic ether ; *viz.*, that it might be a decomposition-product of a hypothetical intermediate substance, carbonyl diurethane, $\text{CO}(\text{NHCOOC}_2\text{H}_5)_2$, which was not obtained, but which he supposed might have been formed and then been decomposed by recrystallization from alcohol or chloroform, losing alcohol and carbon dioxide, and giving allophanic ether.

I varied the conditions of Loeb's reaction somewhat, using undiluted phosgene, and, in order to fulfil the above equation, equal molecules of phosgene and urethane were brought into action. 5 grams phosgene and 4 grams urethane were heated in a sealed tube to 75° for half an hour. When the tube was opened the escaping gas was collected in a nitrometer over sodic hydrate solution. The gas burned with the greenish flame of ethyl chloride. The contents of the tube were then rinsed into a flask with a small amount of benzene and cold, dry ligroïn added. A small amount of a colorless oil (A) was precipitated. Its color resembled that of the other urea chlorides. A part of this oil was added to aniline. The reaction with aniline was very violent and a white solid was obtained. The substance was washed with dilute hydrochloric acid and, recrystallized from hot water and from dilute alcohol, it melted sharply at 106°. Analysis showed it to have the composition $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$.

¹ Loeb : Ber. d. chem. Ges., 19, 2344.

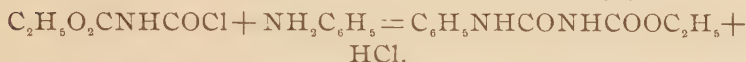
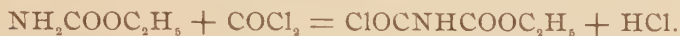
² Gattermann : *loc. cit.*

I. 0.2563 gram substance gave 31.3 cc. moist nitrogen at 741.7 mm. and 21°.

II. 0.2159 gram substance gave 0.454 gram CO₂ and 0.1162 gram H₂O.

	Calculated for C ₁₀ H ₁₂ N ₂ O ₃ .	Found.
N	13.46	13.62
C	57.69.	57.35
H	5.77	5.98

The formula C₁₀H₁₂N₂O₃ corresponds to that of phenylallophanic ether, which could have been formed as follows :



Stojenten,¹ however, who prepared phenylallophanic ether, by the action of ethoxal chloride on monophenyl urea, gives its melting-point as 120°. Another quantity of the above compound was, therefore, prepared and purified by dissolving in sodic hydrate and precipitating it in the filtrate with hydrochloric acid and then recrystallizing the dry substance from ether and ligroïn. It still melted sharply at 106° and the analyses confirmed the composition C₁₀H₁₂N₂O₃.

I. 0.1653 gram substance gave 0.3492 gram CO₂ and 0.0868 gram H₂O.

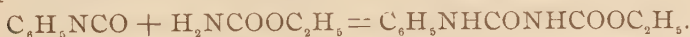
II. 0.1605 gram substance gave 0.3388 gram CO₂ and 0.0849 gram H₂O.

	Calculated for C ₁₀ H ₁₂ N ₂ O ₃ .	I.	Found.	II.
C	57.69	57.61		57.57
H	5.77	5.83		5.87

In view of the discrepancy between the melting-point found by Stojenten and by myself it was decided to prepare phenylallophanic ether synthetically.

Synthesis of Phenylallophanic Ether, C₆H₅NHCONHCOOC₂H₅.

—It was expected that phenyl isocyanate would readily take up urethane and give phenylallophanic ether,

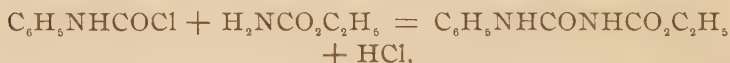


It was found, however, that phenylisocyanate and urethane

¹ J. prakt. Chem. [2], 32, 18.

react only with great difficulty and in a different manner. Molecular quantities were heated to 55° for one hour, and to 160° for one hour; but in no case could allophanic ether be obtained. A mixture of two substances, one melting at about 173° and the other at about 195° , was formed; but these were not further examined; they are probably cyanuric acid derivatives.

A much smoother reaction results if chlorformanilide, $C_6H_5NHCOCI$, the hydrochloric acid addition-product of phenyl isocyanate, is substituted for the latter. 1.5 grams chlorformanilide (1 mol.) and 0.86 gram urethane (1 mol.) were heated to 100° for half an hour. The contents had still a strong odor of isocyanate, but solidified on cooling. The substance was purified by precipitation from alkaline solution and recrystallized from alcohol. The phenylallophanic ether obtained according to the equation,



melted sharply at 106° , and when this synthetic product was mixed with the compound $C_{10}H_{12}N_2O_3$ above referred to its melting-point was not changed. This compound is, therefore, phenylallophanic ether, and the low melting-point is undoubtedly the correct one.¹ Stojenten's phenylallophanic ether was separated from phenylparabanic acid (melting-point 208°) by fractional precipitation, and it is possible that he mistook a mixture for pure phenylallophanic ether.

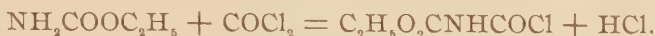
In order to show that the oil (*A*) from which phenylallophanic ether was obtained by means of aniline was not a mixture simply of unchanged urethane and phosgene, which could give phenylallophanic ether according to the equation,



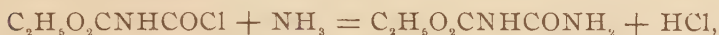
but contained chlorformylurethane, I dissolved a mixture of aniline and urethane in benzene, and added phosgene. The mixture reacted very violently, and carbanilide (melting-point 235°) was obtained, but not a trace of phenylallophanic ether. This proves that the formation of phenylallophanic ether in

¹ *Vide* analyses.

the above reaction with aniline is due to the presence of a chloride, $C_2H_5O_2CNHCOC\bar{C}l$, *chlorformylurethane*, which is formed from phosgene and urethane, as follows :



The presence of chlorformylurethane in the oil *A* was confirmed by converting it by means of ammonia into allophanic ether. The oil *A*, as shown below, contains a very small quantity of allophanic ether, from 10 grams phosgene and 8 grams urethane, half a gram of allophanic ether being obtained. If the oil *A* be divided into two equal portions and dry ammonia be passed into one portion dissolved in benzene, this will give about 6 grams allophanic ether (melting-point 192°), while the other portion, treated in exactly the same way, but without passing ammonia into it, gives only about half a gram of allophanic ether. The allophanic ether is formed as follows :



confirming the presence of chlorformylurethane in the oil *A*.

Besides this substance, the oil *A* contains at least two others. A part of this oil obtained from the first action of phosgene on urethane was left in a desiccator. On standing, this soon became somewhat turbid, and a white solid gradually formed until it consisted of a semi-solid mixture. Water was carefully added, and the mixture extracted with cold ether. From this ether-extract was obtained a small amount of a white crystalline compound which was recrystallized from ether and ligroïn and melted at 107° .

I. 0.1582 gram substance gave 18.8 cc. moist nitrogen at 755.2 mm. and 16.5° .

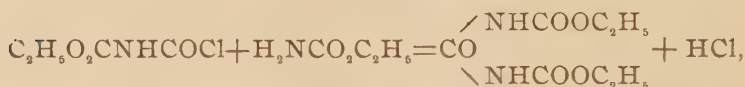
II. 0.1900 gram gave 0.2902 gram CO_2 and 0.1046 gram H_2O .

	Calculated for $C_7H_{12}N_2O_5$.	I.	Found. II.
N	13.73	13.78	
C	41.18		41.66
H	5.88		6.10

The analysis show this substance to have the composition $C_7H_{12}N_2O_5$, corresponding to carbonyldiurethane,



It is formed by the action of the chloride $\text{C}_2\text{H}_5\text{O}_2\text{CNHCOC}_2\text{H}_5$, on a second molecule of urethane,

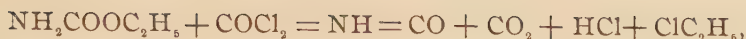


and is the carbonyldiurethane, which Loeb thought might be formed in his reaction, as an unstable intermediate product, and, on being recrystallized, give allophanic ether with loss of carbon dioxide and alcohol, but which had never been obtained before this.

Carbonyldiurethane is, as a matter of fact, a very stable substance. It suffers no decomposition on being recrystallized from any organic solvent or from water. It was heated in a sealed tube with a benzene solution of hydrochloric acid to 75° – 80° for half an hour without change. Carbonyldiurethane cannot, therefore, be considered as an intermediate product in the formation of allophanic ether, as supposed by Loeb, but is one of the final products of the action of undiluted phosgene on urethane.

In the oil *A* there is a small quantity of a third substance, as already mentioned, *viz.*, allophanic ether. It remained after the carbonyldiurethane had been extracted with ether, and was recrystallized from alcohol, and identified by its melting-point (192°) which remained unchanged, when the substance was mixed with synthetic allophanic ether. Since carbonyldiurethane is perfectly stable and is not converted into allophanic ether under the conditions described, the formation of allophanic ether is best explained as follows: Besides acting on the amide group of urethane, phosgene, in a secondary reaction, splits off alcohol from urethane, the cyanic acid formed uniting at once with the liberated hydrogen chloride, giving chlorformamide. This in turn yields with a second molecule of urethane allophanic ether,¹

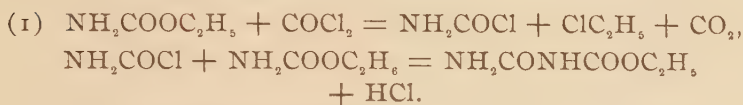
¹ Gattermann: *Loc. cit.*



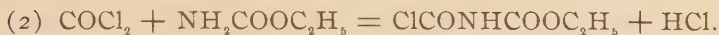
This view is strongly supported by the fact that allophanic ether is obtained from urethane, indifferently by using a number of similar chlorides as thionyl chloride,¹ phosphorus oxychloride,² and, as a by-product, even in the action of benzoyl chloride on urethane,³ where the main product is also benzoylurethane, $\text{C}_6\text{H}_5\text{CONHCOOC}_2\text{H}_5$, as with phosgene. The above explanation satisfies all of these cases.

The action of phosgene on urethane is, therefore, threefold, as may be briefly summarized by the following equations :

To a limited extent we have



To a far greater extent we have



This chloride, being also quite reactive, acts on a second molecule of urethane, so that we have also



Carbonyldiurethane, $\text{CO}(\text{NHCOOC}_2\text{H}_5)_2$.—If in accordance with the last two equations two molecules of urethane be taken to one of phosgene, and the mixture heated to 85° for half an hour, the yield of diurethane is very largely increased. The best yield was obtained as follows: To two molecules of urethane and from one to two molecules of pyridine⁴ was added one molecule of phosgene, contained in a loosely-stoppered tube so as to prevent any action taking place, before sealing the larger tube. The mixture was heated to 85° for thirty minutes, and the contents washed out with a small quantity of water. The water dissolved the pyridine and the pyridine hydrochloride, precipitating nearly all the carbonyldiurethane in a very pure condition. About eight grams diurethane was obtained from ten grams phosgene by

¹ Schroeter and Levinsk : Ber. d. chem. Ges., **26**, 2171. ² Vide p. 23, (this dissertation.)

³ Pechmann and Vanino : Ber. d. chem. Ges., **28**, 2383.

⁴ Vide Pechmann and Vanino : *loc. cit.*

this method. Carbonyldiurethane consists of white plates, and is very soluble in all the organic solvents except ligroïn. It is also readily soluble in hot water and in alkalies.

Silver Carbonyldiurethane, $\text{AgOC} \begin{array}{l} \nearrow \text{NCOOC}_2\text{H}_5 \\ \searrow \text{NHCOOC}_2\text{H}_5 \end{array}$. —From the solution of carbonyldiurethane in alkalies a silver salt can be prepared by precipitating with silver nitrate. The silver salt contains only one atom of silver to each molecule of carbonyldiurethane; my attempts to make it take up two atoms of silver were all unsuccessful. If the compound be dissolved in dilute caustic potash solution containing two molecules potassic hydrate, or a little more than one molecule, the white precipitate which is produced by each drop of silver nitrate solution is at once mixed with the brown oxide of silver. With the ammonia solution of carbonyldiurethane silver nitrate gives no precipitate.

The best method for preparing the pure silver salt I found to be the following: Diurethane was dissolving in dilute caustic potash solution containing a trifle less than one molecule potassic hydrate. Silver nitrate solution in excess was then added with constant stirring. A bulky, gelatinous precipitate, which is very difficult to wash, is thus formed. The mixture was, therefore, left standing in a dark place for twelve hours; the precipitate remained perfectly white. It was then filtered, and washed with cold water and dried in a desiccator. The dry salt was powdered and again washed very thoroughly with cold water, being kept in the dark as much as possible. By this method I obtained the salt pure, and very little colored. A small amount of alkali is liable to cling to it with the greatest tenacity, and cannot be removed from the freshly prepared, gelatinous salt, either by cold or by hot water. The salt is, besides, somewhat soluble in hot water, and to some extent decomposed by it. 4.9 grams of this pure salt was obtained from 4 grams carbonyldiurethane.

I. 0.2488 gram substance gave 0.2441 gram CO_2 and 0.0858 gram H_2O .

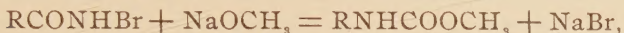
II. 0.3191 gram substance gave 26.4 cc. moist nitrogen at 740.2 mm. and 27.5° .

III. 0.3918 gram substance gave 0.13673 gram Ag.

	Calculated ¹ for $C_7H_{11}N_2O_8Ag$.	Found.
C	27.04	26.76
H	3.54	3.83
N	9.01	8.92
Ag	34.66	34.90

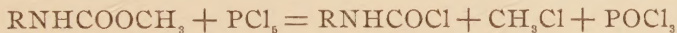
The results obtained in the experiments described in this paper may be summarized as follows.

(1) The reaction



is quite as general as the analogous reaction of alkalis on acid bromamides, and should be quite as useful in the preparation of urethanes as is the reaction of Hofmann in the preparation of amines. The introduction of negative groups into the radical R does not prevent the "Beckmann rearrangement" of the acid bromamides by sodium methylate with the formation of urethanes, and in no case was direct substitution of the bromine atom effected even to a slight extent. This result is in entire accord with the results of Hoogewerff and Van Dorp with aqueous alkalis. The introduction of positive groups, as far as determined by the single case where such a bromamide was examined, has no more influence than that of negative groups.²

(2) The reaction of phosphorus pentachloride on urethanes according to the equation



is also general in the urethanes of the aromatic amines.

The above two reactions together give easy methods for preparing chlorformanilides and isocyanates. The chlorformanilides thus prepared are often much more reactive than the corresponding isocyanates, as shown in the synthesis of phenylallophanic ether, and can be used with advantage in their place.

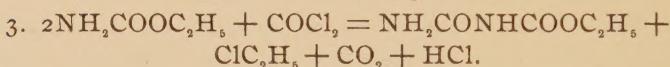
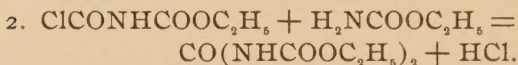
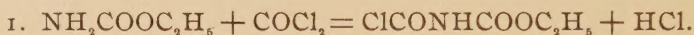
(3) With free urethane, $NH_2COOC_2H_5$, phosphorus pentachloride splits off ethyl chloride and a carbamide chloride is

¹ NOTE.—Mr. F. B. Dains, working under the direction of Dr. Stieglitz, is studying the constitution of this silver salt, and has already obtained an alkyl derivative corresponding to the constitution indicated.

² The investigation on the effect of positive groups is being continued in this laboratory.

formed; but the reaction is not so simple as with the aromatic urethanes; the phosphoric chloride most likely enters the amide group, giving phosphoric acid derivatives of chlorformamide.

(4) Phosgene and urethane when brought together in molecular proportions react simultaneously in three different ways:



The first two reactions can be regulated to a large extent by adding an excess of one or the other of the reacting substances. The third reaction, on the other hand, occurred to a small extent in all the reactions of phosgene on urethane as it apparently does in the action of any acid chloride on urethane.

The above investigations were pursued under the direction of Dr. Stieglitz, and I wish here to express my sincere appreciation of the thoughtfulness with which he guided and assisted me in the work.

